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TETRACARBON METALLOCARBORANES 7. COBALT SYSTEMS DERIVED FROM (C--ETC(U)

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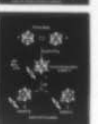
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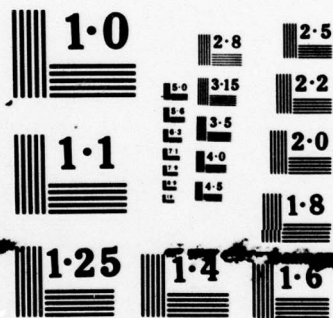
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Tetracarbon Metallocarboranes. 7.¹ Cobalt Systems Derived from
(CH₃)₄C₄B₈H₈. Synthesis and Interconversion of 11-, 12-, and 13-Vertex
Nido Cages

William M. Maxwell and Russell N. Grimes*

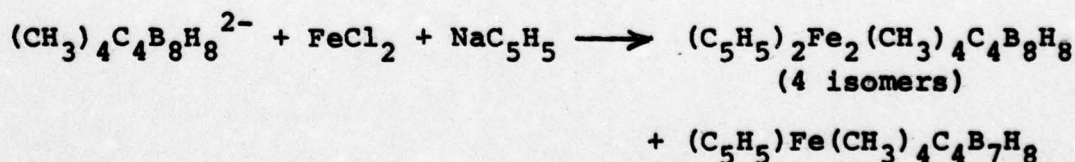
Abstract. Further studies of the novel structural chemistry that has been encountered in carbon-rich metallocarboranes are described. The preparation, isolation, and characterization of new nido-metallocarboranes containing four skeletal carbon atoms is presented, and mechanisms are proposed for their formation. The insertion of cobalt into (CH₃)₄C₄B₈H₈ via reaction with (η⁵-C₅H₅)Co(CO)₂ under uv light produced (η⁵-C₅H₅)Co(CH₃)₄C₄B₇H₇, isomer I, and (η⁵-C₅H₅)Co(CH₃)₄C₄B₆H₆, isomers I and II. The same CoC₄B₇ isomer was obtained from the closo, nido-[(CH₃)₂C₂B₄H₄]Co[(CH₃)₂C₂B₃H₅]⁽⁻⁾ ion by oxidative fusion of the ligands followed by reaction with CoCl₂, NaC₅H₅, and O₂. Treatment of the (CH₃)₄C₄B₈H₈²⁻ dianion with CoCl₂, HCl, and O₂ generated (η⁵-C₅H₅)Co(CH₃)₄C₄B₇H₇, isomer II, σ-[(η⁵-C₅H₅)Co(η⁵-C₅H₄)]-(CH₃)₄C₄B₈H₈, and (η⁵-C₅H₅)Co(CH₃)₄C₄B₈H₈, of which the first two products have been structurally characterized by X-ray studies. From ¹¹B and ¹H FT NMR, IR, and low- and high-resolution mass spectroscopic data, and from electronic, synthetic, and mechanistic considerations, structures are proposed for the remaining CoC₄B₆, CoC₄B₇, and CoC₄B₈ cage isomers. A third isomer of (η⁵-C₅H₅)Co(CH₃)₄C₄B₇H₇ was obtained on rearrangement of isomer I at 140°.

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Introduction

Synthetic and structural investigations of four-carbon carborane and metallocarborane cage systems have been a continuing project in our laboratory,² through which we are attempting to develop systematic relationships between skeletal electron population, molecular geometry, and mechanisms of cage formation and rearrangement. The preparative routes to tetracarbon metallocarboranes as they have developed thus far, are of two main types: fusion of dicarbon metallocarboranes to produce dimetallic four-carbon cages^{1,3-6} (schematically, $2 C_2B_nM \longrightarrow C_4B_{2n}M_2$), and insertion of metal groups into tetracarbon carboranes.⁷ The second route has been employed to generate 12-, 13-, and 14-vertex metallocarboranes of iron, cobalt, nickel, molybdenum, and tungsten from neutral $(CH_3)_4C_4B_8H_8$ or its dianion, e.g.,



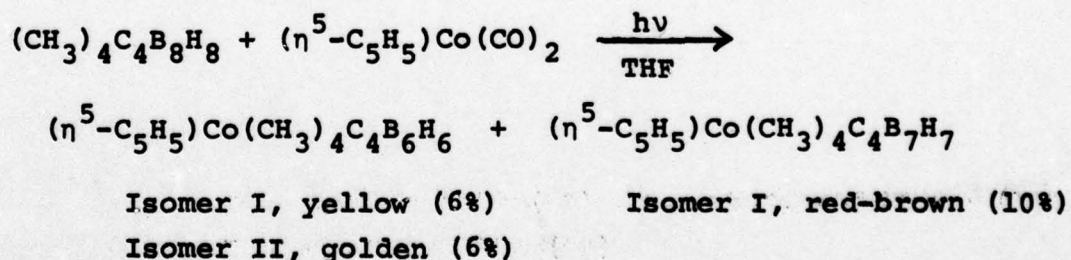
We have previously described the synthesis and rearrangements of the iron species, together with X-ray crystallographic studies of several key compounds.^{7,8} Although one might simplistically expect the insertion of $(\eta^5-C_5H_5)Co^{2+}$ units into $(CH_3)_4C_4B_8H_8$ or its dianion to parallel that of iron and hence yield similar

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stereochemistry, this is not the case. The cobalt reactions, which are the subject of this paper, in fact follow a quite different course and generate a series of tetracarbon cobaltacarboranes which are structurally distinct from their iron counterparts.

Results and Discussion

Direct Insertion of Cobalt into Neutral $(CH_3)_4C_4B_8H_8$. The reaction of $(CH_3)_4C_4B_8H_8$, a colorless, air-stable solid, with $(\eta^5-C_5H_5)Co(CO)_2$ in tetrahydrofuran (THF) under ultraviolet light at $27^\circ C$ produced several cobaltacarboranes which were isolated on thin-layer silica plates in air (the same products were obtained in comparable yields by heating the reagents in THF at 80° for 12 hr).



The new compounds were characterized from their ^{11}B and 1H FT NMR, IR, and unit- and high-resolution mass spectra (Tables I-IV), which serve to establish the molecular formulas but do not uniquely define the cage geometries. Although crystal structures of these

materials are not yet available, sufficient information about the structures and reactions of closely related molecules is in hand to permit tentative assignments.

In Figure 1 we indicate a likely reaction pathway with proposed structures of the products. The carborane substrate, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, exists in solution as an equilibrium mixture of two isomers,³ one of which (A) is isolable in the solid state and has been crystallographically characterized.⁹ The remaining isomer (B) has not been structurally defined but the structure shown in Figure 1 was recently proposed.¹⁰ Although this geometry is not crucial to the structural assignments of the cobaltocarborane products given below, the inclusion of both $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ isomers in Figure 1 emphasizes the fact that cobalt insertion may well occur in either or both isomeric forms (or in a common intermediate); presently available data do not allow us to identify the specific substrate(s) on which metal attack occurs.

As suggested in Figure 1, the major product 1 [$(\eta^5\text{-C}_5\text{H}_5)\text{Co} \circ (\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ (isomer I)] forms via net replacement of one BH unit in $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ with a $\text{Co}(\eta^5\text{-C}_5\text{H}_5)$ group. The cage geometry proposed for this species is that of a structurally characterized compound,¹¹ $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{-OC}_2\text{H}_5$, with the ethoxy group replaced by hydrogen. A comparison of FT NMR spectra for the two species is compatible with this assignment; thus, the ^{11}B spectrum⁶ of the ethoxy compound exhibits B-H doublets at δ 11.1, 1.2, -7.9, and -16.8 and a B-OC₂H₅ singlet at δ -9.1, with relative areas

1:2:2:1:1, which can be compared with the data for the unsubstituted species in Table I. The proposed structure for 1 is, moreover, closely related to both the A and B geometries of the carborane precursor, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, and can be formally derived from either isomer by replacing B(1)-H with $\text{Co}(\text{C}_5\text{H}_5)$ and stretching the appropriate framework C-C interactions to produce cage-opening.

Perhaps the strongest support for the assigned structure of 1 is provided by its synthesis independently from the closo, nido-complex $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$ as described below. This alternative route to 1 is envisioned as occurring via oxidative fusion of the two carborane ligands to generate a C_4B_7 cage into which cobalt is incorporated.

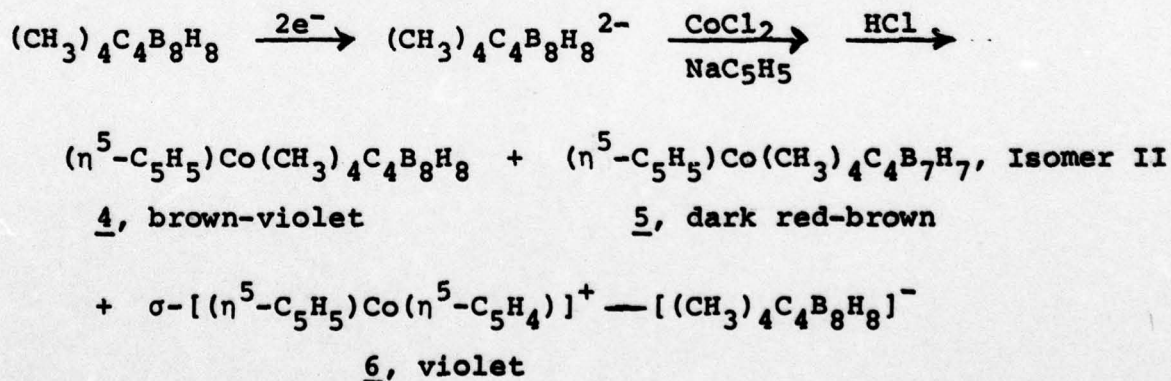
The geometries of the remaining products, isomers I and II of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$, are less certain, but the most likely structures are depicted in Figure 1. Both proposed geometries have mirror symmetry, in agreement with the ^{11}B and ^1H FT NMR data, and both are 11-vertex icosahedral fragments in accordance with the presence of 26 skeletal electrons. Unlike the situation in 12-vertex, 28-electron cages, where distortion from icosahedral symmetry is required by the presence of two "extra" electrons but no single geometry dominates,¹¹ the obvious choice for an 11-vertex, 26-electron species is an icosahedron with one missing vertex; this is, of course, the structure of the 1,2- and 1,7- $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ ("dicarbollide") ions¹² which are isoelectronic with the CoC_4B_6 systems.

Several arrangements for the cobalt and carbon atoms in an 11-vertex icosahedral fragment are possible, in addition to those proposed in Figure 2. However, the NMR spectra indicate a mirror plane in each isomer, requiring in turn that the number of carbon atoms on the open face be zero, two, or four; since framework carbons tend to adopt low-coordinate vertices on the open face in open-cage carboranes and metallocarboranes,^{13,14} it is likely that both isomers contain C_4B rather than C_2B_3 or B_5 faces. There are, moreover, readily envisioned pathways for conversion of the CoC_4B_7 to the two proposed CoC_4B_6 species, each of them involving loss of one BH group and movement of a C-CH₃ unit into the vacated vertex (Figure 1). One other possible structure which contains a C_4B open face and still retains the mirror plane, has the cobalt in position 10 (numbering as in compound 1). However, since this structure has no carbons adjacent to cobalt and its formation from the CoC_4B_7 species is more difficult to visualize, it appears a less attractive possibility.

Insertion of Cobalt into the $(CH_3)_4C_4B_8H_8^{2-}$ Ion. The neutral carborane $(CH_3)_4C_4B_8H_8$ is easily reduced by sodium naphthalide to the dinegative ion as described in an earlier publication.⁷ Treatment of this dianion with iron or nickel reagents produces MC_4B_7 , MC_4B_8 , and $M_2C_4B_8$ metallocarborane systems, several of which have been crystallographically characterized,^{7,8} but the structure of the $(CH_3)_4C_4B_8H_8^{2-}$ ion itself has never been established. This is a question of some significance since $(CH_3)_4C_4B_8H_8^{2-}$ is a 12-

vertex, 30-electron arachno species, cage-isoelectronic with $C_2B_{10}H_{12}^{4-}$ and with the hypothetical ion $B_{12}H_{12}^{6-}$; in principle,¹⁴⁻¹⁶ one would expect such a system to adopt a geometry based on a 14-vertex closo cage (bicapped hexagonal antiprism¹⁷) with two missing vertices, but structural data have not been available. Unexpectedly, the present investigation provided us with an answer to this question in the form of a σ -bonded derivative of $(CH_3)_4C_4B_8H_8^{2-}$ which we were able to characterize structurally.

The reaction of $(CH_3)_4C_4B_8H_8^{2-}$ ion with $C_5H_5^-$ and $CoCl_2$ in THF at 25°, followed by acidification with aqueous HCl and isolation of the products on thin-layer silica plates in air, gave small quantities of three compounds. Spectroscopic data on the products



4-6 (Tables I-IV) did not permit structural assignments, but X-ray crystal structure analyses of 5¹⁸ and 6¹⁰ have been obtained. In addition, a recent X-ray study¹⁹ of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, Isomer I, supplies us with a strong clue to the structure of 4 since

$[(C_6H_5)_2PCH_2]_2Ni$ and $(C_5H_5)Co$ are each formal 2-electron donors^{15,16} to skeletal bonding and the nickel complex is thus an electronic analogue of 4.

As shown in Figure 2, compound 6 is a cobaltocenium-substituted derivative of the $(CH_3)_4C_4B_8H_9^-$ ion, derived from the $(CH_3)_4C_4B_8H_8^{2-}$ dianion by addition of H^+ and replacement of $H\cdot$ with $(C_5H_5)Co^{III} \subset (C_5H_4)^+$ at a boron vertex. A full description of the structure determination, and a discussion of mechanisms of transition metal insertion into the dianion, have been presented elsewhere.¹⁰ For present purposes, it will be noted that 6 contains a bridging CH_3CH group which spans two mutually nonbonded boron atoms, and that the "extra" hydrogen in the molecule resides on this unique carbon atom. It is assumed that when this proton is absent, as in the $(CH_3)_4C_4B_8H_8^{2-}$ dianion, the bridging carbon moves fully into the cage framework as shown in the Figure.

On the basis of structural information presently available, we postulate that complexes 4, 5, and 6 form as depicted in Figure 2. Attack of a cobaltocenium radical cation²⁰ on $(CH_3)_4C_4B_8H_8^{2-}$ followed by protonation yields 6 as suggested above; however, reaction of the dianion with $Co(\eta^5-C_5H_5)^{2+}$ leads to incorporation of the metal into the cage, forming the 13-vertex nido species 4 which can undergo loss of boron to produce the 12-vertex system 5. The proposed structure of 4 has not been established, but is consistent with the NMR data and is supported by two additional observations: it is isostructural with the

known NiC_4B_8 system mentioned above, and its conversion to 5 appears straightforward via elimination of a BH group and formation of a carbon-carbon link. From the locations of skeletal carbon atoms in 4, 5, and 6 we infer that 4 and 6 are formed from different isomers of the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ dianion. The presence of dianion isomers is strongly suggested by the plethora of metallocarborane isomers that are obtained on complexation with iron and nickel reagents;⁷ mechanistic schemes for the fluxional interconversion of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ isomers have been described in another context.¹⁰

The established structure of 5 further extends the list of structural types that have been found among tetracarbon species. As shown, the molecule has four- and five-sided open faces which are separated by a C-CH₃ group that might be described as bridging three cage atoms; however, this unique carbon atom has no bound hydrogen and hence is not a methylene-type bridge as found in 6. It will be noted that 5 is yet another example of a 12-vertex, 28-electron (nido) framework¹¹ and constitutes the fifth distinct structural class to be identified among such systems. The X-ray investigation of 5 and its structural and mechanistic implications will be the subject of a future article.¹⁸

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{B}_7\text{H}_7$, Isomer I, from Closo, Nido- $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$. The mixed-ligand complex $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$, 7, and some chemistry based on it have been described in an earlier paper,⁴ and its structure was

established via an X-ray study of a cobaltocenium-substituted derivative.²² In the present investigation, 7 was treated with sodium hydride in THF to remove the metal-bound proton⁴ and the resulting anion was allowed to react with CoCl_2 and NaC_5H_5 , generating compound 1 (identical to the species obtained from $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ ion) in 14% yield (Figure 3). An alternative procedure employing n-butyllithium as the deprotonating agent and glyme as the solvent, gave the same product.

The formation of 1 from 7 provides additional support for the proposed structure of 1 (vide supra), and also furnishes another example of oxidative ligand fusion.² Thus, the merger of formal $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ and $(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5^{2-}$ ligands to form a $(\text{CH}_3)_2\text{C}_2\text{B}_7\text{H}_7^{2-}$ species from which the neutral monocobalt complex 1 is generated, is analogous to the fusion of two $(\eta^5\text{-C}_5\text{H}_5)\text{CoR}_2\text{C}_2\text{B}_3\text{H}_4^-$ ions to form $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{R}_4\text{C}_4\text{B}_6\text{H}_6$ ($\text{R} = \text{CH}_3$ or H)⁵, or of two $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ ligands to produce $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{3,4}$ (other examples have been cited elsewhere²).

The mechanism(s) of these fusion processes, including the conversion of 7 to 1, has not been established in detail, but a plausible model is developing from continuing synthetic and structural studies. Thus, a recent crystallographic structure determination of $[\text{2,3}-(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2^{24}$ has revealed that the $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ ligands have a mutually staggered conformation which is evidently retained during fusion since the same relationship exists⁹ between the $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ units in the fused carborane product, $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. Further discussion of this question appears elsewhere.^{2,24}

Thermal Isomerization of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, Isomer I.

In an effort to incorporate an additional metal atom into the framework of 1, that complex was heated with excess $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ in nonane at 140° . However, the only isolable product was

a new isomer of the starting material. The structure of this compound, isomer III (8), has not been assigned, but the ^{11}B and ^1H FT NMR spectra indicate the absence of any planes or axes of symmetry. A crystallographic study will clearly be required in this case.

Conclusions

An extraordinary variety of cage structures, many of them without precedent, has been encountered in our exploration of tetracarbon metallocarborane chemistry. It is clear that electronic and steric effects combine to produce a large number of accessible cage geometries. In terms of framework electron count,^{15,16,23} most of these systems contain either $2n + 4$ or $2n + 6$ electrons (where n is the number of vertex atoms) and

are expected to adopt structures of the nido and arachno types, respectively. The basic problem, as this and earlier work makes clear, is that within these categories so many distinct cage geometries are capable of stable existence. Even in $(2n + 2)$ -electron systems, where one expects closo polyhedra, open-cage structures that are thermodynamically unfavorable can be stabilized by kinetic effects, as we have previously found in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ system.⁸

Despite the complex stereochemistry exhibited by the tetracarbon systems, the basic patterns of structure and mechanism are gradually emerging as new findings become available. The number of discrete types of polyhedral framework that can be adopted by isolable products is surely limited, and it is reassuring that we have already found duplication in several instances; for example, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8$ ⁷ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$ (isomer VII)⁵ exhibit the same cage geometry (though with different heteroatom arrangements),

while other known isopolyhedral pairs consist of the complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{-OC}_2\text{H}_5$ ¹¹ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ (isomer V)^{1,5}, and isomers I and V of the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ system.⁸

Further work in this area is continuing.

Experimental Section

Materials. Tetra-C-methyl-tetracarbadodecaborane(12), $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, was prepared from the complex $[2,3\text{-(CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$ as described elsewhere.³ All other reagents were commercially obtained reagent grade compounds.

Spectra and Chromatography. ¹¹B and ¹H pulse Fourier transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E mass spectrometer, and high resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high resolution measurements were performed under chemical ionizing conditions in methane or argon-water. Thin- and preparative-layer chromatography was conducted in air on pre-coated plates of silica-gel F-254 (Brinckman Instruments, Inc.).

Reaction of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$. The carborane (35 mg, 0.17 mmol) and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (41 mg, 0.23 mmol) were placed in a quartz reaction vessel and 2 ml of THF was added by distillation. The mixture was irradiated with a Sears 275 watt sun lamp under a nitrogen atmosphere for 96 hr. The reactor was then opened to the atmosphere and stirred for 3 hr after which methylene chloride was added to the black product mixture and the mixture was filtered through silica gel. The resulting filtrate was placed on a silica gel TLC plate (0.5 mm) and was repeatedly developed in hexane. Four significant bands were obtained: band 1, colorless $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, 9 mg; band 2, yellow $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$, isomer I, $R_f = 0.32$, 2 mg; band 3, golden $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$, isomer II, $R_f = 0.16$, 2 mg; band 4, red-brown $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, isomer I, $R_f = 0.04$, 4 mg (10% yield based on carborane consumed). The mass spectrum of each metallocarborane product exhibited a strong envelope corresponding to the parent ion, with a profile consistent with the assigned formula. Further characterization was based on ^{11}B and ^1H FT NMR and IR spectra, and on high resolution mass measurements (Tables I-IV).

The products $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ (isomer I) and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ (isomer I) were also obtained in yields comparable to those given above, by heating an equimolar solution of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ in n-nonane at 110°C for 2 hr.

Preparation of Metallocarboranes from the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ Ion. To 95 mg (0.49 mmol) of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ in vacuo at -196° , were added through a glass frit THF solutions of NaC_5H_5 (4.10 mmol) and sodium naphthalenide (0.95 mmol). The reaction vessel was allowed to come to ambient temperature with stirring, during which the solution color changed from dark green to a clear light pink. To this solution was slowly added from a sidearm addition flask CoCl_2 (351 mg, 2.70 mmol) with constant stirring. The solution color quickly darkened to deep brown with a reddish tint. The solution was stirred for 12 hr after which the reactor was opened to the atmosphere and 0.25 ml of concentrated aqueous HCl in 20 ml of THF was added and the solution stirred for an additional 8 hr. The resulting solution was filtered and solvent removed from the filtrate by distillation in vacuo. The residue was extracted with CH_2Cl_2 , filtered through silica gel, placed on silica gel TLC plates, and developed in benzene, giving three main bands. Band 1, pale yellow, contained $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, naphthalene, and traces of unidentified metallocarboranes as shown by mass spectroscopic evidence. Band 2 ($R_f = 0.72$) was dark violet and contained two compounds which were subsequently separated by repeated development on a silica gel column in 20% benzene/hexane and characterized as $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, isomer II, 2 mg, and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$, 3 mg. Band 3 (from the original TLC development) was violet $\sigma\text{-(}\eta^5\text{-C}_5\text{H}_5\text{)Co(}\eta^5\text{-C}_5\text{H}_4\text{)-(CH}_3\text{)}_4\text{C}_4\text{B}_8\text{H}_8$, 6 mg. The three new compounds

exhibited strong parent envelopes in their mass spectra and were further characterized spectroscopically (Tables I-IV) and by X-ray crystallographic analyses of the first and third products.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, Isomer I, from Closo, Nido- $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$. To a solution of the reactant complex (40 mg, 0.16 mmol) in 2 ml glyme was added 0.17 mmol of $\eta\text{-C}_4\text{H}_9\text{Li}$ in hexane. The mixture rapidly became dark red with gas evolution; to it were then added 0.65 mmol of NaC_5H_5 in 3 ml glyme and 200 mg (1.54 mmol) of solid anhydrous CoCl_2 . The resulting solution was stirred for 6 hr and then opened to the air. The dark green solution was filtered into 5 ml of THF which had been acidified with 0.25 ml of concentrated aqueous HCl. This solution was stirred, solvent removed, the black-green residue extracted with CH_2Cl_2 and filtered through silica gel. The filtrate was placed on a silica gel TLC plate and developed in hexane. Two major bands were obtained, consisting of starting metallocarborane and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, isomer I (identical with the product obtained in the reaction of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ together with numerous colored but extremely weak bands. The yield of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ was 6.5 mg (13% based on the initial quantity of metallocarborane reagent).

The same product was obtained in 14% yield by treatment of the same metallocarborane reagent with NaH in THF followed by addition of excess CoCl_2 and NaC_5H_5 in THF at room temperature.

Thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, Isomer I, with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$. A 5-mg sample of the metallocarborane and 100 mg of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ were placed in a 5 ml round bottom flask and 1 ml n-nonane was added by distillation in vacuo. The solution was heated under N_2 at 110°C for 2.5 hr, after which spot TLC analysis in 20% benzene-hexane revealed the presence of a new red-brown compound together with starting metallocarborane. The reaction mixture was then heated at 140°C for 18 hr, at which point TLC analysis in 20% benzene-hexane exhibited an intense orange spot ($R_f \sim 0.2$) corresponding to a new compound, but very little of the original metallocarborane. Following removal of volatiles by vacuum distillation, the solid residue was dissolved in CH_2Cl_2 , placed on a 0.5 mm silica gel TLC plate, and eluted in 35% benzene/hexane to give one major band characterized as orange $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, isomer III ($R_f = 0.40$, 2.5 mg, 50% yield) plus a small amount (<1 mg) of the original isomer I.

Acknowledgments. This work was supported by the Office of Naval Research.

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- (20) The formal oxidation state of cobalt is +2 in the starting reagent but +3 in the isolated metallocarborane products; the oxidation of cobalt may take place during workup of the products in air, but probably occurs at least partially at an earlier stage via disproportionation of cobalt species during the reaction (metallic cobalt is frequently obtained²¹ in cobaltacarborane syntheses involving CoCl_2).
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Table I. 32.1 - MHz ^{11}B FT NMR Data^a

Compounds	δ , ppm ^b (J, Hz)	Rel Areas
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_7$ Isomers	16.6(144), 2.0(150) ^{c,d} , -3.8(140), -8.7(112), -12.9(136), -18.7(144)	1,2,1,1,1,1
Isomer I (<u>1</u>)		
Isomer II (<u>5</u>)	23.6(156), 11.7(147), -0.8(136), ^c -2.8(147) ^c , -17.6(146), -29.1(146)	1,1,3,1,1
Isomer III (<u>8</u>)	12.8(140) ^c , 11.0(140) ^c , 3.7(137), -8.2(156), -12.7(127)	2,1,2,1,1
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ Isomers		
Isomer I (<u>2</u>)	4.9(156), -9.7(150), -23.4(140)	3,2,1
Isomer II (<u>3</u>)	-3.0(160), -10.3(150), -32.1(154)	3,2,1
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (<u>4</u>)	12.7(112) ^c , 9.5(146) ^c , 2.3(166) -7.5(166), -11.5(120), -15.1(136) ^c , -18.5(127) ^c	1,1,1,2,1,1,1
$(\text{C}_5\text{H}_5)\text{Co}(\text{C}_5\text{H}_4)-(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (<u>6</u>)	14.9(150), [-6.0, -11.9, -13.4] ^e , -22.2 ^f , -47.2(146)	1, [5], 1, 1

^aAll spectra were obtained in CDCl_3 solution. ^bParts per million relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with positive sign indicating shift to lower field (less shielding). ^cJ values estimated from overlapped resonances. ^dAsymmetric peak with shoulder on upfield side.

^eChemical shifts obtained from proton-decoupled spectrum; $J_{\text{H-B}}$ not measurable due to heavy overlap in the undecoupled spectrum.

^fB-cobaltocenium resonance.

Table II. 100-MHz ^1H FT NMR Data^a

Compound	δ , ppm ^b (rel area)	Assignment
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ Isomers		
Isomer I (<u>1</u>)	4.98(5) 2.50(3), 1.92(3), 1.77(6)	C_5H_5 CH_3
Isomer II (<u>5</u>)	5.15(5) 1.83(3), 1.72(3), 1.36(6) ^c	C_5H_5 CH_3
Isomer III (<u>8</u>)	5.08(5) 2.30(3), 1.76(3), 1.66(3), 1.61(3)	C_5H_5 CH_3
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ Isomers		
Isomer I (<u>2</u>)	5.10(5) 1.82(6), 1.47(6)	C_5H_5 CH_3
Isomer II (<u>3</u>)	4.81(5) 1.46(6), 1.41(6)	C_5H_5 CH_3
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (<u>4</u>)	5.00(5) 2.64(3), 2.08(3), [1.39, 1.36] (6)	C_5H_5 CH_3
$(\text{C}_5\text{H}_5)\text{Co}(\text{C}_5\text{H}_4)-(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (<u>6</u>)	5.41(5) 5.58(2), 5.30(2) [1.57, 1.55] (9), 0.82(3)	C_5H_5 C_5H_4 CH_3

^aAll spectra were obtained in CDCl_3 solution. ^bParts per million relative to $(\text{CH}_3)_4\text{Si}$ with positive sign indicating shift to lower field. ^cArea-6 CH_3 peak was just resolvable on ^{11}B -decoupling at 32.083930 Hz, which produced line narrowing.

Table III. Infrared Absorptions (CH_2Cl_2 solution vs. CH_2Cl_2 , cm^{-1})

- | | |
|----------|--|
| <u>1</u> | 2928 m, 2853 w, 2523 vs, 1831 w, 1428 m, 1373 m, 1250 w, 1108 m, 1013 s (doublet), 968 w,sh, 938 w, 863 w, 828 s. |
| <u>2</u> | 2950 w,sh, 2920 m, 2855 m,sh, 2530 s, 1450 m, 1420 w, 1390 w, 1375 w, 1245 w,broad, 1035 w, 1008 w (doublet), 960 w, 928 m, 905 w, 847 w, 838 m, 739 w. |
| <u>3</u> | 2940 m, 2870 w, 2580 s, 2520 m,sh, 1422 m, broad, 1380 w (doublet), 1248 w, broad, 1170 w, 1105 w, 1080 w, 1065 w, 1020 w, 990 w, 935 w, 865 w, 820 s. |
| <u>4</u> | 2930 s, 2860 m, 2540 vs, 2440 m,sh, 1725 w, broad, 1430 m,broad, 1375 w, 1250 m, broad,1120 w, 1070 m, 1020 w, 995 w, 902 m, broad, 838 s, 690 m, broad. |
| <u>5</u> | 2955 w,sh, 2925 m, 2860 w, 2525 s, 1430 m, broad, 1373 w, 1250 m, broad, 1005 w, 833 m. |
| <u>6</u> | 2950 w, 2930 m, 2860 m, 2540 s, 1725 w, br, 1430 m, broad 1250 m, 1005 m, 895 w, 845 w, 700 s. |

Table IV. High Resolution Mass Measurements^a

Compound	Formula	Mass	
		Calcd	Obsd
<u>1</u> ^b	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^1\text{H}_{24}^+$	316.1862	316.1866
	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^1\text{H}_{25}^+$	317.1940	317.1923
<u>2</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_6^1\text{H}_{23}^{+c}$	304.1690	304.1721
	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_5^{10}\text{B}^1\text{H}_{23}^{+c}$	303.1725	303.1731
<u>3</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_6^1\text{H}_{24}^+$	305.1769	305.1769
<u>4</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_8^1\text{H}_{26}^+$	329.2111	329.2096
<u>5</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^1\text{H}_{25}^+$	317.1940	317.1942
<u>6</u>	$^{59}\text{Co}^{12}\text{C}_{18}^{11}\text{B}_8^1\text{H}_{30}^+$	393.2424	393.2424

^aMass of P + 1 ion (protonated parent ion) obtained in methane under chemical ionizing conditions. ^bSpectrum obtained in argon-water. ^cParent (P) ions.

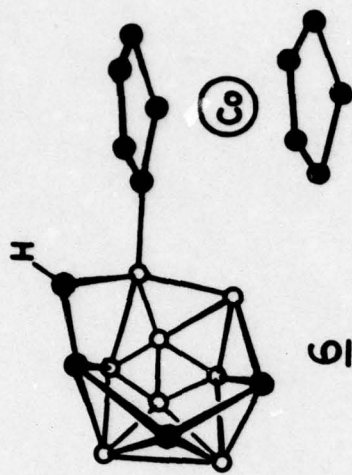
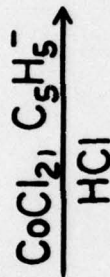
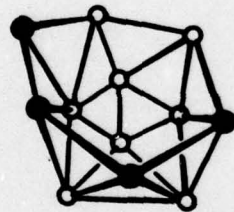
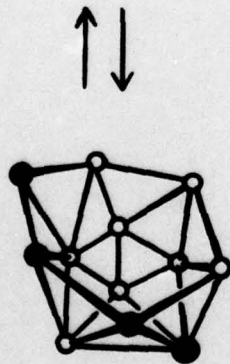
Figure Captions

Figure 1. Scheme for the preparation of 11- and 12-vertex nido-cobaltacarboranes from neutral $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. The structure of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (isomer A) is established;⁹ those of isomer B, $(\eta^5\text{-C}_5\text{H}_5)\text{Co} \curvearrowright (\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ (isomer I), and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ (isomers I and II) are proposed from NMR and other evidence. Both isomers of the CoC_4B_6 system have mirror symmetry.

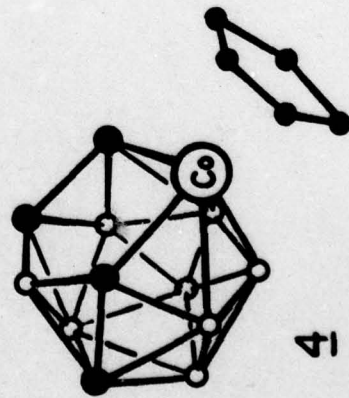
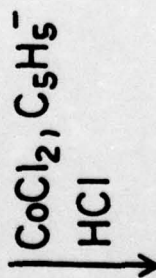
Figure 2. Scheme for the preparation of $\sigma\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^5\text{-C}_5\text{H}_4)]^+ \text{-} (\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^-$ (6), $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (4), and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ (5) from the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ dianion. The structures of 5 and 6 are known from X-ray studies,^{18,10} and that of 4 is based on the established structure¹⁹ of $[(\text{C}_6\text{H}_5)_2\text{PCH}_2]_2\text{Ni}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. The proposed interconversion of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$ isomers shown here is described in detail elsewhere.¹⁰

Figure 3. Alternate synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ (isomer I) from closo, nido- $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$ (7). The conversion probably involves oxidative fusion of the $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ and $(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5^{2-}$ ligands in 7 to form $(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$, with subsequent addition of cyclopentadienylcobalt to the latter species.

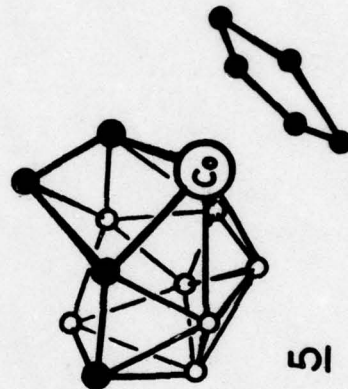
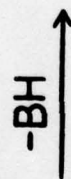
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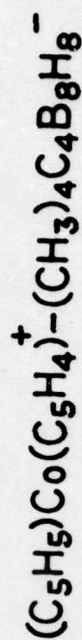
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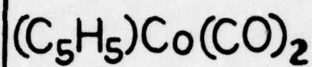
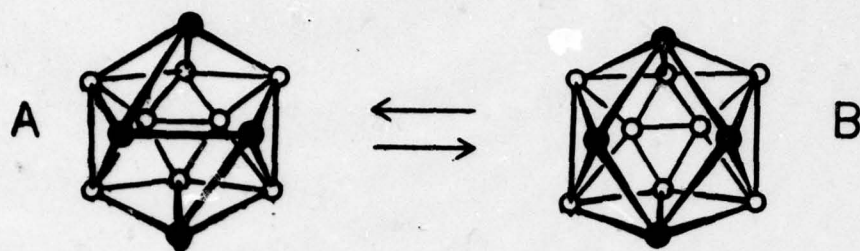
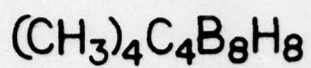


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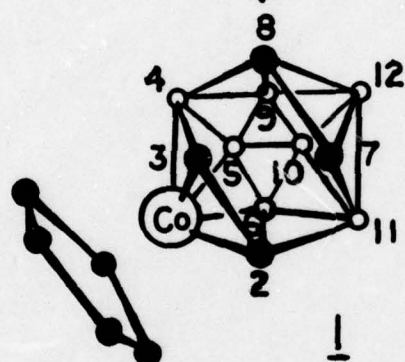


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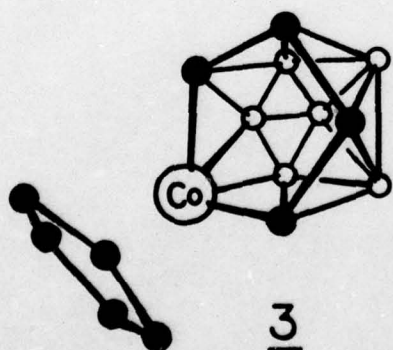


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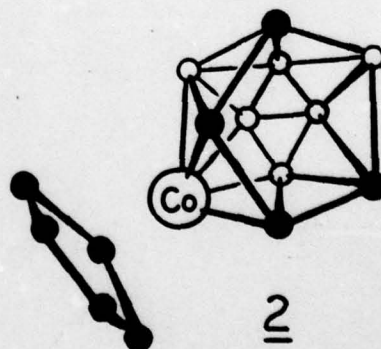


$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$
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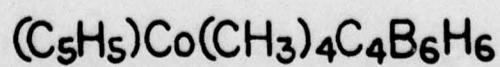
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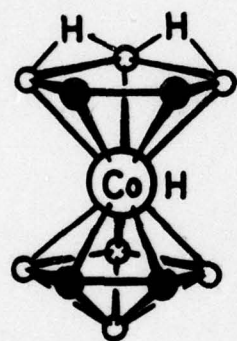


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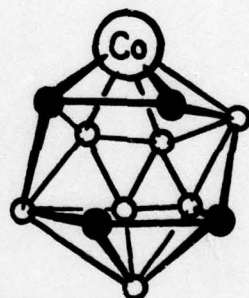
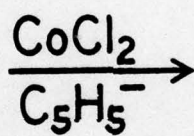
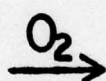
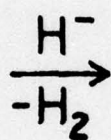


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ISOMER I





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